Recovery of Technetium and Iodine from Spent ATW TRISO Type Fuels

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Accelerator Transmutation of Waste Program
Final Report for WBS 1.24.02.02

Abstract

The Accelerator Transmutation of Waste (ATW) program is being developed to determine the feasibility of separating and transmutating the transactinides (Pu-Cm) and long-lived fission product (^{99}Tc and ^{129}I) from spent LWR fuel. Several types of ATW fuels have been suggested to transmutate the Pu-Cm fraction including TRISO type fuels. An ATW TRISO fuel would consist of a Pu-Cm oxide kernel surrounded by several layers of pyrolytic carbon, a layer of SiC, and an outer layer of pyrolytic carbon. Processing of the spent ATW fuel would involve the crush, burn, and leach approach used on normal TRISO fuels. This report describes experiments that determine the potential behavior of the two long-lived fission products, ^{99}Tc and ^{129}I, in this processing. Iodine can be removed and trapped during the burning of the carbon from the fuel. Some technetium may volatilize in the latter stages of the burn but the bulk of it will have to be recovered after dissolution of the oxide residue.

Introduction

The Accelerator Transmutation of Waste (ATW) program is being developed to determine the feasibility of separating and transmutating the transactinides (Pu-Cm) and long-lived fission product (^{99}Tc and ^{129}I) from spent LWR fuel. The separated transactinides would be processed and fabricated into an ATW fuel while the technetium and iodine would be fabricated into elemental and salt type targets, respectively. This approach would help with the disposal of spent commercial fuel. In addition, since the residual waste after ATW treatment will have much lower levels of these long-lived species this process may improve the performance and acceptability of geologic disposal of nuclear waste. A roadmap for the Accelerator Transmutation of Waste (ATW) was submitted to Congress in 1999.[1] This document gave an overall view of the ATW concept and program.

The ATW fuel requirements[2] have been delineated as the following: (1) ATW fuel and targets must be fabricable with remote processes, (2) ATW fuel and target forms must be compatible with fuel recycle processes, (3) the blanket fuel must maintain the fissile material in a predictable configuration and location in the transmuter, (4) the blanket fuel must provide robust containment for fission products, and (5) the blanket fuel must retain a coolable geometry during operation. Several types of fuels have been suggested to meet these requirements including the TRISO type fuel developed by the General Atomic Company (GA).

A number of years ago, the United States of America and the Federal Republic of Germany conducted programs on the development and demonstration of High Temperature Gas Cooled Reactor (HTGR) technology. The lead organization in the United States was the General Atomic Company.[3] The fuel used in this approach consisted of small particle (usually less than 1 mm) that had a center core or kernel of fissile fuel coated with a layers of pyrolytic carbon and silicon carbide. Fissile fuel forms/types and coatings varied. Those that had silicon carbide sandwiched between

layers of pyrolytic carbon were designated TRISO fuels. TRISO fuels are capable of sustaining very high burnup values but require good fuel design and fabrication.

Thermal, chemical and mechanical methods have been considered for reducing and breaking up the spent graphite fuel for reprocessing.[4] Themoshock at 2500-3000°C embrittles the graphite and SiC coatings and leads to reactions of the fuel kernels (and fission products) with these component. Numerous carbides and intercalation compounds of carbon are formed. The subsequent separation chemistry became very complicated. In addition, insurmountable materials and corrosion problems were realized by this approach.

A pure chemical disintegration occurs by introducing chemical vapors of potassium, cesium, bromine or ferric chloride into the graphite matrix. This leads to distortion of the graphite matrix and disintegration. The chief reasons for not using these methods are the corrosion problems along with the sophisticated engineering required. In addition the use of alkali metal requires inert atmosphere systems. However, these problems are not unknown to the molten salt processing.[5] This may be an alternative processing option for graphite ATW fuels especially since the volume of the feed stream will be much smaller than the processing scale for HTGR fuels.

Dry mechanical crushing and grinding has been the only procedure that has been practical for the head-end processing of HTGR fuels. The process is more sophisticated than it sounds. A collaborative effort between GA and the Federal Republic of Germany worked out many of the details of the crushing process and the subsequent processing (see below).[3]

Several options have been proposed to treat the crushed fuel including high temperature chlorination, acid leaching, and burn and leach. Dry chlorination at 1000°C is required to get satisfactory reaction rates for uranium and thorium. Unfortunately, other fission products also chlorinate and the process has presented serious corrosion problems.

Direct leaching of the uranium from the ground fuel is a slow process and recoveries are less than desirable. In addition the acids attack the graphite and produce mellithic acid ($C_{12}O_{12}H_6$) or similar compounds which then interfere with the PUREX processing of the acidic leach solution.

The reference and most technically advanced process has been a two stage crushing/burning process. The burners used are fluidized bed reactors that use a mixture of O_2 and CO_2 to aid the burning; bed temperatures typically run at ~900°C.[3,6] The first crush/burn step is done to remove the matrix graphite that surrounds the particles. Crushing is done to produce suitably sized particles for a fluidized bed burner. The SiC coated particles leaving the burner are then crushed and burned to get rid of the inner carbon layers, the crusher gap is set to prevent the crushing of the kernal.[3] The solids that remained are dissolved (leached) to prepare a feed for normal PUREX processing. The general processing of graphite fuel is shown in Figure 1.[7] Note that once the crush burn leach process is complete normal PUREX processing begins.[7-9] A scheme similar to Figure 1 could be used for treating spent ATW type TRISO fuels.

This crush, burn, and leach approach has not paid particular attention to the recovery of technetium and iodine. For example, attention in the reprocess for iodine has been basically one of trapping and insuring no release to the environment. The reprocessing of TRISO type ATW fuel particles will require >95% recovery of the LLFPs. The volatilization of iodine from graphite HTGR or ATW fuels is expected to be

Insert Fig 1. **Proposed Treatment of TRISO Fuels**

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similar because the chemical state of iodine should be I_2 in both cases.[7,10] Technetium on the other hand may be in the metallic state associated with noble metal inclusions or, if the oxygen potential is high enough, it may exist as an oxide.[7,10]

This report will describe our experiments to determine the fate of technetium and iodine during the burning and leaching process. The goal was to determine if >95% of the technetium and iodine could be recovered from the processing of TRISO type ATW fuels so that they could be formulated into targets for transmutation into stable ruthenium (^{100}Ru) and xenon (^{100}Xe) isotopes, respectively.

Small Particle Fuels—BISO and TRISO Particles

There have been two types of small particle fuels reported for study in gas-cooled nuclear reactor systems, the more common TRISO (TRIstructural ISOtropic) particles consisting of four layers and the less common BISO (Bistructural ISOtropic) particles.[9] Both types of particles have been used in the early study of these fuel types for the high temperature gas-cooled reactor (HTGR). BISO particles are fissile material coated with a relatively porous buffer layer of carbon and then coated with a dense coating of pyrolytic carbon. The TRISO particles have in addition a silicon carbide coating placed between the two layers of pyrolytic carbon. The silicon carbide layer provides a barrier to enhance retention of the metallic fission products. In the past the BISO particles have been used with thoria (ThO_2) kernels. TRISO particles have had some variations on the fuel types, and the carbide type, primarily zirconium carbide replacing silicon carbide. Figure 2 is a schematic diagram of the BISO fuel particles and Figure 3 is the diagram for the TRISO fuel particles.[9]
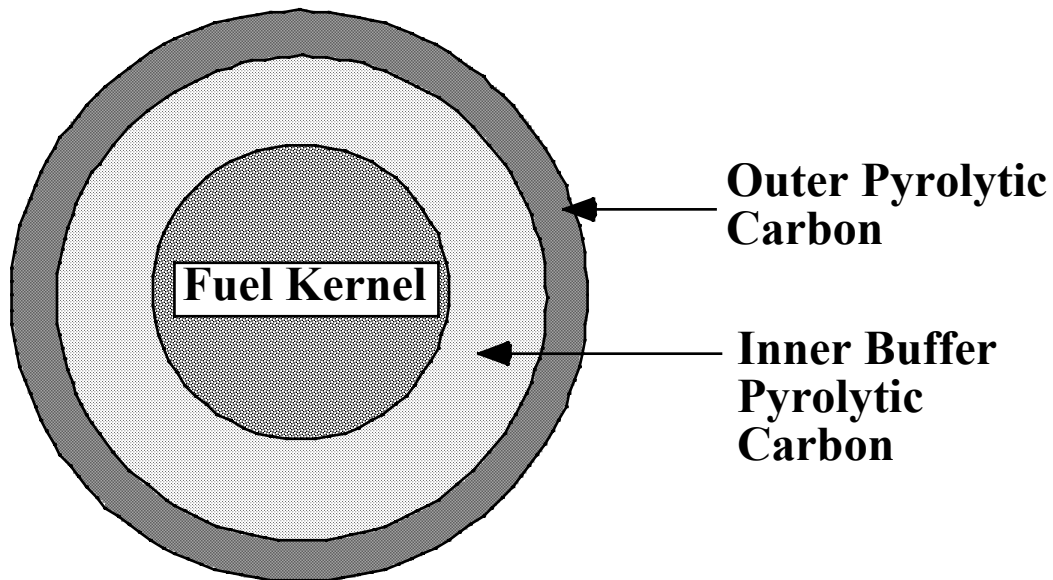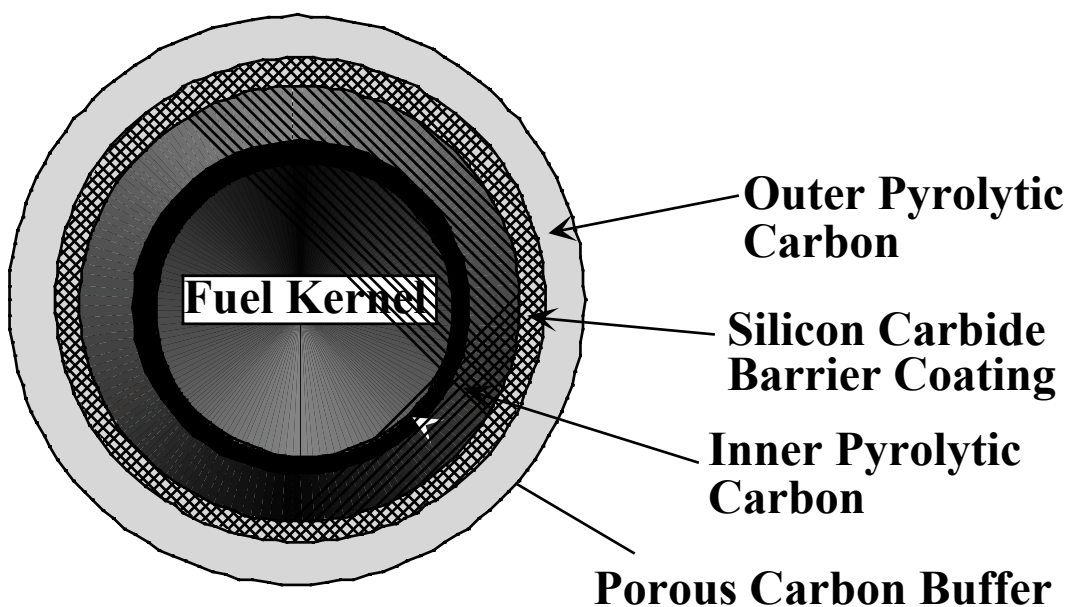

Figure 1. BISO fuel particle.

Figure 2. TRISO fuel.

The TRISO fuel particles were designed to retain the fission products more efficiently using pyrolytic carbon buffers and silicon carbide coatings. For ATW application the kernel of a TRISO fuel would be a mixture of transactinide elements destined for transmutation. After transmutation the spent ATW fuel would be processed by a scheme similar to that shown in Figure 1.

TRISO Simulants

We were unable to obtain any type of TRISO fuel particles (uranium, enriched or depleated, thorium) from GA to use as a simulant for ATW fuel. Because of this we prepared several simulants. A crushed TRISO fuel simulant (CTS) was prepared based on the composition of the Ft. St. Vrain HTGR fuel particles shown in Figure 3. These particles have a UO_2: PyC: SiC ratio of 2:2:1. The simulant substitutes La_2O_3 for UO_2 and activated carbon (AtC) for the pyrolytic carbon (PyC). The activated carbon was crushed and sieved to between 0.6 and 0.15 mm. The La_2O_3: AtC: SiC ratio is 2:2:1. Samples of CTS were spiked with ^{125}I (as I^-) and ^{95m}Tc (as TcO_4^-). Only about 40% of the iodine activity sorbed onto the simulant while >90% of the technetium sorbed. Figure 4 shows mass and activity profiles verses time for burning the spiked CTS simulant samples in a muffle furnace. The mass or activity profiles measures the ratio of the weight or activity of the sample at any time divided by the initial weight or activity. Burning of the CTS simulant should leave only La_2O_3 and SiC as the residual products. The mass and activity profiles for technetium parallel each other and the greatest changes
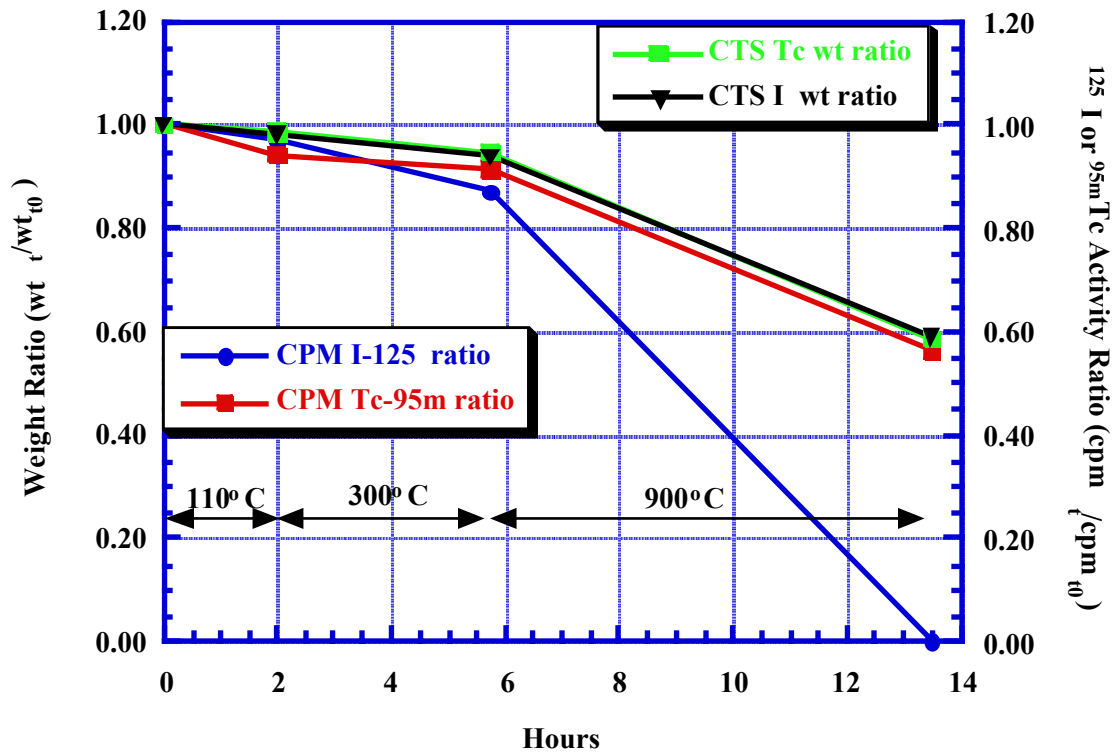
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Figure 4. Burn of ^{125}I and ^{95m}Tc Traced Crushed TRISO Simulant (CTS).

occur during the 900°C burn. This behavior is generally true for iodide but the iodide is somewhat more volatile. While all the ^{125}I is lost after 7.5 hours at 900°C only ~33% of the technetium is volatilized. Only minor changes in the both factors for each element occur at temperatures ≤ 300°C.

Figure 5 shows a similar experiment except that there are macro amounts of iodine (~6mg I/g CTS) and technetium-99 (~0.5mg ^{99}Tc/g CTS) sorbed on to the CTS along with the tracers. The technetium sorption (as TcO_4^-) is almost quantitative. The iodides (natural NaI and ^{125}I$^-$) were converted, with H_2O_2, to I_2 for sorbing onto the CTS. Sorbing I_2 on to the simulant is somewhat difficult as most of it volatilizes readily under mild heating (i.e., heat lamp). In the muffle furnace, at 300°C, almost 66% of the I_2 is lost in 4 hours. In the prior experiment very little I$^-$ is lost at this temperature. The more rapid volatilization in this experiment is due to the molecular iodine speciation. Thus the speciation of iodine in the TRISO type ATW fuel will be important. Iodine is present as I_2 in regular TRISO fuel and there is no reason to expect it to be different in the ATW fuel.[5] If present as I_2 a clean separation from the ATW fuel and technetium could be achieved by burning at 300°C. Burning at 900°C would separate technetium. At the macro level technetium volatilizes in parallel with the weight loss profile. The mechanism for technetium volatilization might occur by an initial reduction of pertechnetate by carbon to TcO_2 and then either an oxidation to Tc_2O_7 or a disproportionation to technetium metal and Tc_2O_7 (bp = 316°C). The metallic technetium would then have go through a re-oxidation by O_2 to TcO_2. Alternatively, since TcO_2

7

sublimes at 900°C this may be the species that volatilizes. A word of caution is needed in reference to these last statements: ATW type TRISO fuel, as in normal TRISO fuels, will most likely have technetium alloyed with Mo, Ru, Rh and Pd.[7,10] Volatilization of technetium from these noble metal inclusions may be more difficult since it will have to migrate to the surface of the alloy and be oxidized to TcO_2 and then to Tc_2O_7.
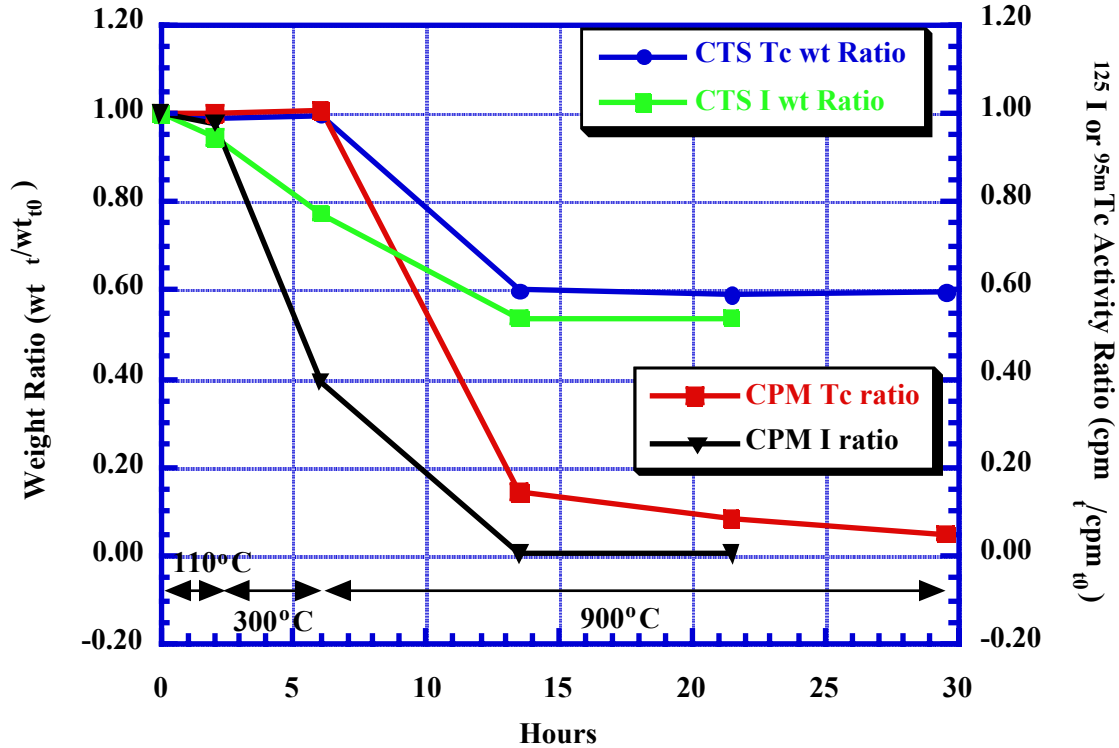
Figure 5. Burn of CTS Simulant Containing Macro Amounts of I_2 and TcO_4^- and Traced with ^{125}I and ^{95m}Tc.

An alternative TRISO simulant was prepared from a sample of ZrO_2 coated with pyrolytic carbon (PyC) that was obtained from Medical Carbon Research Institute (Austin TX). The weight percent ZrO_2 in this material is 50%. The material was crushed and sieved to between 0.6 and 0.15 mm and mixed 4:1 with SiC. The simulant formulation is therefore ZrO_2:PyC: SiC at a ratio of 2:2:1. Figure 6 compares the burning of this simulant (Zr) against CTS simulant for samples that were both covered (c) with a crucible lid or uncovered. There was surprisingly little difference between the CTS samples; both samples rapidly lost their carbon at 500°C whether they were covered or not. Pyrolytic carbon does not appear to burn until the temperature exceeded 500°C. The greater stability of pyrolytic carbon is also reflected in the difference between the covered and uncovered samples. Exposure to air greatly facilitates the burning of this allotropic form
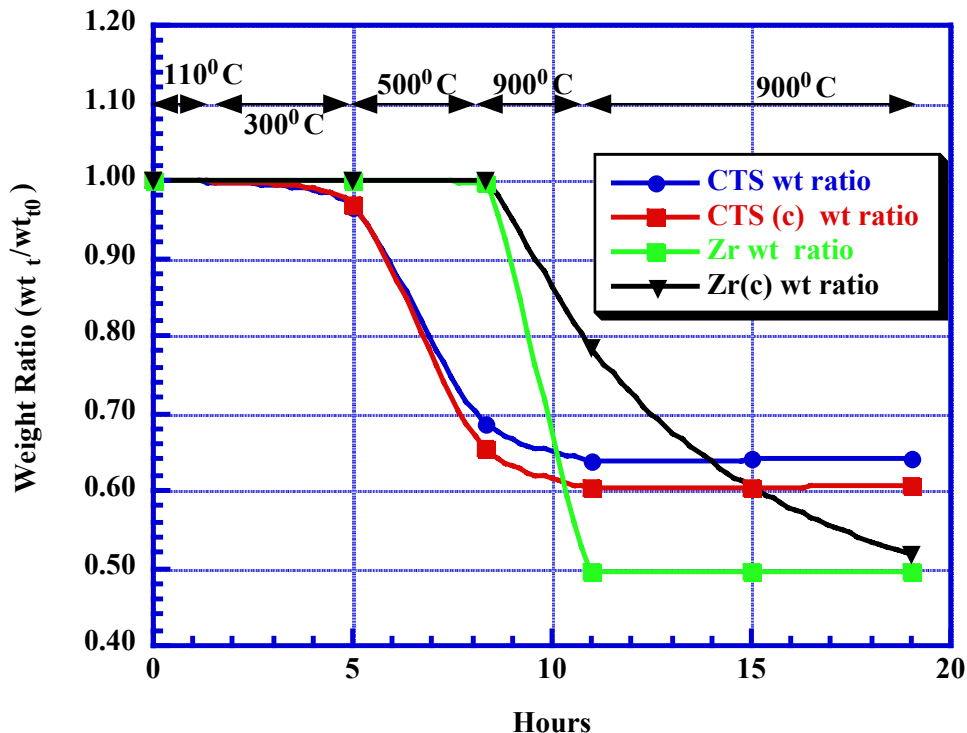
Figure 6. Burning of CTS and Zr Simulants Covered (c) and Uncovered.

of carbon. Based on this result it would be wise to use pyrolytic carbon in any simulant that attempts to mimic the behavior of TRISO type fuels. For this reason a new type of simulant (ZCSL) was formulated to have a ZrO_2:PyC:SiC:La_2O_3 ratio of 1:1:1:1. Figure 7 compares the weight and activity ratios for the burn of this simulant to the CTS simulant. Both simulants had macro amounts of I_2 or TcO_4^- loaded onto them. Smaller incremental increases in temperature were used in this experiment. The activated carbon in the CTS simulant burns quite well at 400°C. The pyrolytic carbon in the ZCSL simulant burns at 600°C. There is a rapid decrease (> 60%) in the ^{125}I activity in both simulants during the first 20 hours of the burn when the temperatures ranged between 300°C to 500°C. This is probably due to the loss of I_2 during this period. After 20 hours the loss of ^{125}I activity slows which may indicate that there is residual I⁻ in the samples. The iodine loss from the ZCSL simulant is not related to the mass loss but to temperature. This probably true for the CTS simulant as well but it is less defined in this experiment. Technetium volatility from both simulants is related to weight loss but there is a definite lag in the volatility relative to the weight loss. Almost all of the carbon needs to be burned off before significant technetium volatility occurs. For example technetium is lost from the CST simulant only during the last 10% of the weight loss. The ZCSL simulant

Insert Fig 7 here

Insert Fig 8 here

is even more extreme. About 15% of the ^{95m}Tc activity is lost over 8 hours at 900°C even though the weight of the simulant appears to be at its final weight. From this behavior it appears that a small amount of residual pyrolytic carbon can have significant effect on the behavior of technetium. On the other hand, after all the carbon has burned away technetium may be in an oxidation state that is slow to volatilize. The consequence of technetium's behavior for processing are that an off-gas system will be required to capture Tc_2O_7 and technetium will have to be leached from the post-burn solid residue.

Figure 8 shows another burn of ZCSL simulant samples containing macro amounts of technetium and iodine (I_2). All the samples displayed a similar weight loss pattern. About 75% of the I_2 was lost in 16 hours followed by a slow loss of almost all their iodide over the next 44 hours. An insignificant amount of technetium was lost over this period. Thus a clean separation of 95% of the iodine can be made by volatilization. The iodine would of course have to be separated from other volatile species (i.e., noble gases, etc.).

The five technetium samples were removed from the furnace at various point during the burn; number 3 after the second 600°C burn (28 hours), number 1 after the first 800°C burn (44 hours), numbers 2 and 4 after the first 900°C burn (61 hours), and number 5 after the second 900°C burn (69 hours). Only 40% of the technetium activity was lost from the latter sample even though it was at 900°C for 16 hours. By comparing the technetium volatility in Figures 7 and 8 there appears to a linear relationship between technetium loss and the time the sample burns at 900°C.

After burning, the five technetium samples were leached with nitric acid. All the samples behaved the same and >95% of the technetium was dissolved from the solid. Another sample of ZCSL containing macro amounts of technetium was burned for 10 hours at 900°C. Sixty-seven percent of the activity was leached from the residue with water. This water soluble activity is probably from soluble pertechnetates, dissolved Tc_2O_7, or possibly solubilized TcO_2. Anhydrous TcO_2, which could be present after the burn, is not expected to be soluble. Surprisingly, very little (<5%) activity is removed from the residue by a subsequent leach with H_2O_2. Thus there appears to be little TcO_2 in the residue. A white solid fraction was separated from a dark fraction in the remaining residue. The activity in the white residue represents about 30% of the insoluble technetium activity. Since the white solid is soluble in nitric acid it is the La_2O_3 part of the simulant and it appears to contain some $La(TcO_4)_3$. Nitric acid dissolves most of the residual activity left in dark residue. Since zirconium oxide is not soluble in HNO_3 it appears that technetium metal may have be present in the sample. As described previously this could occur by reduction of pertechnetate to TcO_2 by the carbon in the simulant followed by a disproportionation reaction to give Tc metal and Tc_2O_7. However, the leaching experiments described above do not give definitive evidence for TcO_2 being in the sample.

References

1. A Roadmap for Developing ATW Technology, DOE Office of Civilian Radioactive Waste Management, DOE/RW-0519, October 1999.

2. Accelerator Transmutation of Waste: Fuel and LLP Target Develop Plan for FY '01 through FY '05 – DRAFT – August 2000. Prepared by the ATW Fuel Development Working Group, D.C. Crawford, Chair.

3. F.A. Schwarz and J. B. Strand, "US/FRG Cooperative HTGR Program Joint Fuel Processing Demonstration JFPD Sequential Operations at General Atomic Company", GA-A16141, UC-86 (February 1981).

4. Norbert G. Hoogen and Erich R. Merz, "Evaluation of Potential Head-End Procedures for Graphite-Containing Fuel Elements", *Nuclear Technolog*y, **61**, 380 (1983).

5. J. Laidler, Argonne National Laboratory(ANL), personal communication and tours of the molten salt processing facilities at ANL (2000-2001).

6. N. D. Holder and C. W. Olsen, "Spent Graphite Fuel Element Processing", General Atomic Project 3261, GA-A16405 (July 1981).

7. P. Groot, E. H. P. Cordfunke, and R.J.M. Konings, "The Chemical Stability of TRISO-Coated HTGR Fuel", Netherlands Energy Research Foundation, ECN-1-94-055, December 1994.

8. L. J. Olguin, "Continuous Solvent Extraction Feed Adjustment for HTGR Fuel Processing", General Atomic Project 3261, GA-A15014 (June 1978).

9. H. H. Yip and L. J. Olguin (work done by H. H. Yip, L. J. Olguin, C. A. Brown, R. Delesdernier, R. G. Wilbourn, A. H. Bond, F. J. Rustay, and G. A. Cook), "Dissolution in HTGR Fuel Reprocessing", General Atomic Project 3261, GA-A15092, UC-77 (August 1978).

10. K. Minato, T. Ogawa, K. Fukuda, M. Shimizu, Y. Tayama, and I. Takahashi, "Fission Product Behavior in TRISO-Coated UO_2 fuel Particles", *Journal of Nuclear Materials*, **208**, 266 (1994).